(54) Title: METHOD AND APPARATUS FOR GAS PURIFICATION

(57) Abstract: This invention comprises an adsorption process for the removal of at least N_2O from a feed gas stream that also contains nitrogen and possibly CO_2 and water. In the process the feed stream is passed over adsorbents to remove impurities such as $CO2$ and water, then over an additional adsorbent having a high N_2O/N_2 separation factor. In a preferred mode the invention is an air prepurification process for the removal of impurities from air prior to cryogenic separation of air. An apparatus for operating the process is also disclosed.

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METHOD AND APPARATUS FOR GAS PURIFICATION

[0001]   This application claims the benefit of US
    provisional applications 60/342,673, filed December 20,
    2001 and 60/384,611, filed May 31, 2002 the entire
    teachings of both are herein incorporated by reference.

FIELD OF THE INVENTION

[0002]   This invention relates to the removal of N_2O,
    hydrocarbons, water vapor and CO_2 from gas streams, and
    more particularly to the removal of impurities from
    air, using adsorptive separation, prior to cryogenic
    separation of air.

BACKGROUND OF THE INVENTION

[0003]   Cryogenic separation of air requires a pre-
    purification step to remove contaminants such as water,
    CO_2 and hydrocarbons from air. In cold sections of the
    separation process (such as heat exchangers and LOX
    sump), water and CO_2 can solidify and block the heat
    exchangers or other components in the distillation
    columns. Acetylene and other hydrocarbons in air
    present a potential hazard. The high boiling
    hydrocarbons can accumulate in the liquid oxygen and
    create an explosion hazard. Thus, those impurities in
    air must be removed in an adsorptive clean-up process
    prior to the cryogenic distillation of air.

[0004]   Nitrous oxide (N_2O) should also be removed from
    air prior to separation. N_2O is currently present in
    air at a concentration of about 300-350 ppb, however,
    this concentration is increasing annually at a rate of
    about 0.3%. Various factors such as emissions from

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motor vehicles, HNO_3 plants, adipic acid and caprolactam plants (both use HNO_3 for oxidation of inorganics) contribute to this growing ambient concentration of N_2O. The presence of greater than 50 ppb of N_2O can be a serious problem for cryogenic air separation units (ASU) because it can form solid deposits in distillation columns. N_2O also decreases the solubility of CO_2 in liquid oxygen, thereby increasing the potential for freezing of CO_2 in the distillation columns. This can result in degraded performance and can even cause blockage of heat exchangers.

[0005]   Air prepurification can be accomplished using pressure swing adsorption (PSA), temperature swing adsorption (TSA) or a combination of both (TSA/PSA) incorporating either a single adsorbent or multiple adsorbents. When more than one adsorbent is used, the adsorbents may be configured as discrete layers, as mixtures, composites or combinations of these. Impurities such as H_2O and CO_2 are commonly removed from air using two adsorbent layers in a combined TSA/PSA process. Normally, a first layer of activated alumina is used for water removal and a second layer of 13X molecular sieve is used for CO_2 removal. Prior art, such as U.S. 4711645, teaches the use of various adsorbents and methods for removal of CO_2 and water vapor from air.

[0006]   Centi et al. (Ind. Eng. Chem. Res., vol. 39, pp 131-137, 2000) studied the behavior of various ion exchanged forms of ZSM5 Zeolites for removal of relatively high concentrations of N_2O (500ppm (parts per million) to 2000ppm) from industrial gas streams.

ZSM5, being a high Si/Al ratio (2-200) zeolite, has less water affinity than its low Si/Al ratio counterparts. The best performance for N_2O removal in Centi's study is shown by Ba and Sr exchanged ZSM5. The paper indicates that in the presence of water, metal exchanged ZSM-5 has better N_2O adsorption properties than lower Si/Al ratio zeolites such as X and Y type zeolites.

[0007]   U.S. 6,106,593 teaches a process, preferably TSA, that uses a three-layer adsorbent bed for successive removal of water, CO_2 and N_2O, wherein the preferred adsorbent is binderless CaX. Other adsorbents such as CaX (with binder), BaX and Na-mordenite are also recommended for the third layer. According to the patent, the criteria for selecting an adsorbent for N_2O removal is a Henry's law selectivity for N_2O compared to CO_2 of 0.49 or more at $30^{\circ}C$ and a Henry's law constant for N_2O adsorption of at least 79 mmol/gm.

[0008]   European patent application EP 0 862 938 teaches the placement of a zeolite adsorbent selected from X-zeolite, Y-zeolite, A-zeolite or mixtures thereof downstream of an alumina adsorbent in a PSA process to remove nitrogen oxides, such as NO, NO_2, N_2O and N_2O_3.

European Patent Application EP 0 995 477 teaches a method of removing at least a portion of N_2O in a gas stream using a type-X zeolite with a Si/Al ratio of 1.0 -1.5 and containing a mixture of $K^+(<35\%)$, $Na^+(1-99\%)$ and $Ca^{2+}(1-99\%)$ cations in various proportions.

[0009]   European Patent Application (EP 1 092 465) teaches a TSA process (sequentially removing H_2O, CO_2 and N_2O and optionally hydrocarbons using a three-layer configuration of adsorbents. A NaLSX adsorbent is

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preferred in the second layer for CO_2 removal. A LSX zeolite (Si/Al=0.9-1.3), preferably CaLSX zeolite, is suggested for N_2O and hydrocarbon removal.

[0010]   European Patent Application EP 1 064 978 teaches the use of BaX zeolite to remove propane, ethylene and N_2O in a PSA or TSA process. The BaX zeolite contains at least 30% barium cations.

[0011]   U.S. 4,156,598 teaches the method of removing N_2O from nitrogen trifluoride by passing the gas through a synthetic zeolite adsorbent, such as sodium or calcium exchanged type X or type A zeolite.

[0012]   U.S. 4,933,158 teaches a method of removing N_2O and CO_2 from nitrogen trifluoride by passing the gas through a thermally treated zeolite selected from the group consisting of analcime, clinoptilolite, mordenite, ferrierite, phillipsite, chabazite, erionite and laumotite.

[0013]   U.S. 4,507,271 teaches the method of removing N_2O from a gas containing hydrogen, nitric oxide and nitrous oxide using A, X or Y zeolite.

[0014]   U.S. 5,587,003 discloses a method for removing substantially all of the CO_2 from air using the adsorbent clinoptilolite.

[0015]   Rege et al. (Chemical Engineering Science, vol. 55, pp 4827-4838, 2000) showed 13X adsorbent to provide better CO_2 removal from air than clinoptilolite. Rege also showed that Ca-exchanged clinoptilolite to have low N_2 adsorption.

[0016]   Catalytic decomposition of the contaminant is another means of removing an undesirable component from a gas mixture. A catalyst/adsorbent can be used much in the same way as described above except that the

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product of decomposition must be either removed as an
additional contaminant or be an acceptable component of
the gas mixture.

[0017]   The prior art has typically derived its solution
to the problem by seeking adsorbents with high N_2O to
CO_2 selectivity. However, given the similar electronic
structure of N_2O and CO_2, and the nearly 1000-fold
difference in gas phase concentration between N_2O and
CO_2 in air, this methodology is difficult to apply.
Thus an improved process and apparatus for the removal
of N_2O and other impurities from air is required.

SUMMARY OF THE INVENTION

[0018]   In a preferred embodiment of the invention, CO_2
and water are removed from the feed air, then an
adsorbent having a high N_2O/N_2 separation factor is
used for N_2O removal. Such adsorbent also has a higher
Si/Al ratio and modest to low N_2O/CO_2 selectivity as
compared to the prior art.

[0019]   In a preferred embodiment, the invention relates
to an adsorption process for the removal of N_2O from a
gas containing N_2O, nitrogen and other components to
produce a product gas, said process comprising passing
said gas over a bed of one or more adsorbents, wherein
at least one of the adsorbents is selected from the
group consisting of clinoptilolite, chabazite and Li-
exchanged zeolite or combinations thereof.

[0020]   In a more preferred embodiment, the gas is air and
the other components include water and CO_2.

[0021]   In one embodiment N_2O is in said gas in an amount
of less than 100ppm.

[0022]   In one embodiment the water and the CO_2 are
          adsorbed on an additional adsorbent prior to the gas
          passing over the clinoptilolite, chabazite or Li-
          exchanged zeolite.

[0023]   In one embodiment the process is an air
          prepurification process.

[0024]   In a preferred embodiment, at least 90% of the N_2O
          in the gas is adsorbed.

[0025]   In one embodiment the Li-exchanged zeolite is LiX.

[0026]   The invention also comprises a process for the
          separation of N2O from a gas stream containing at least
          N_2O and nitrogen, said process comprising passing said
          gas stream over a bed of adsorbent having a working
          capacity ΔN_2O of greater than or equal to 3.56×10^{-4} at
          IBL.

[0027]   In a preferred embodiment the gas stream is air.

[0028]   In a preferred embodiment the adsorbent is
          selected from the group consisting of clinoptilolite,
          chabazite and Li-exchanged zeolite or combinations
          thereof.

[0029]   In a preferred embodiment the gas stream contains
          less than 100ppm N_2O.

[0030]   The invention also comprises an adsorption
          apparatus for the removal of N_2O from a gas containing
          N_2O, nitrogen and other components, said apparatus
          comprising one or more beds of at least a first
          adsorbent, wherein said first adsorbent is an N_2O
          selective adsorbent selected from the group consisting
          of clinoptilolite, chabazite and Li-exchanged zeolite.

[0031]   In a preferred embodiment the other components in
          the gas include H_2O and CO_2, and said apparatus further

contains one or more additional adsorbents for the adsorption of H_2O and CO_2, and wherein the additional adsorbents are upstream of said first adsorbent.

[0032]   The process and apparatus of the present invention provide surprisingly superior N_2O removal efficiency over prior art processes and systems.

BRIEF DESCRIPTION OF THE DRAWINGS

[0033]   Other objects, features and advantages will occur to those skilled in the art from the following description of preferred embodiments and the accompanying drawings, in which:

[0034]   Fig. 1 is a schematic diagram of the breakthrough test apparatus;

[0035]   Fig. 2 is a graph of N_2O breakthrough curves for NaX(2.5) for N_2O/N_2 and N_2O/He;

[0036]   Fig. 3 are nitrogen isotherms for certain adsorbents;

[0037]   Fig. 4 are breakthrough curves to show initial breakthrough (0.05 ppm level);

[0038]   Fig. 5 illustrates IBL N_2O loading for certain adsorbents (IBL:Initial breakthrough loading- N_2O adsorbed per unit weight of adsorbent at the 50 ppb breakthrough);

[0039]   Fig. 6 is a schematic of an adsorption system useful for practicing the invention.

[0040]   Fig. 7a illustrates a bed from a conventional prepurifier with an added layer for N_2O removal in accordance with the invention.

[0041]   Fig. 7b illustrates a bed from a prepurifier with a first layer for water removal and a downstream mixed layer for CO_2 and N_2O removal.

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[0042]   Fig. 7c illustrates a bed from a prepurifier with
a first layer for water removal and a downstream mixed
layer for hydrocarbon and N_2O removal.

[0043]   Fig. 7d illustrates a bed from a prepurifier with
a first layer for water removal a second layer for CO_2
removal, a third layer for removal of hydrocarbons and
a final layer for N_2O removal.

DETAILED DESCRIPTION OF THE INVENTION

[0044]   The invention is based upon first recognizing the
critical components (N_2O/N_2) to be separated, then
isolating these critical components in an adsorption
zone within the adsorber and finally selecting an
adsorbent that can efficiently affect the separation.
The general problem to be solved is the removal of ppb
levels ($\approx$ 350-400 ppb) of N_2O from a mixture of air
containing other contaminants (including at least CO_2
and H_2O) prior to air separation by cryogenic means.
In a process for removal of contaminants from a gas
mixture by adsorption, it is common to adsorb
contaminants successively in the order of decreasing
adsorptivity and/or decreasing selectivity with respect
to a chosen adsorbent. The effectiveness of such a
process can often be improved by using a combination of
adsorbents, configured in layers or mixtures, to
enhance the removal of each contaminant, i.e. by
selecting particular adsorbents to achieve maximum
adsorptivity and or selectivity of each contaminant
relative to the gas mixture. The use of different
adsorbents disposed in layers in the adsorber is well
known in the art.

[0045]   The selection of an adsorbent to remove a
          particular contaminant depends upon many factors, e.g.
          the type and composition of both the targeted
          contaminant and other gases in the mixture at the point
          of removal within the adsorber, the relative
          selectivity of the adsorbent for the contaminant(s) and
          non-contaminants, and the loading capacity of the
          adsorbent for the contaminant.

[0046]   In a preferred embodiment of the invention, an
          adsorbent bed is first configured to remove
          substantially all of the CO_2 and H_2O from the feed
          stream (e.g. air) prior to removing N_2O. N_2O is then
          subsequently removed the partially purified feed
          stream. The present invention differs from the prior
          art in that an adsorbent is selected for the N_2O
          separation such that the adsorbent has both a high
          $\Delta N_2O/\Delta N_2$ separation factor and a high ΔN_2O (in the
          presence of high N_2 concentrations) capacity. Natural
          clinoptilolite, natural chabazite and LiX are preferred
          embodiments for N_2O removal from gases, particularly
          air, in accordance with the invention. With the
          addition of the N_2O adsorbent, the combination of all
          the adsorbents in the bed removes at least 90% and
          preferably all of the N_2O from the feed stream. Thus,
          the purified stream contains preferably less than 100
          ppb (parts per billion), more preferably less than 50
          ppb and most preferably less than 10ppb N_2O at the
          local stream conditions

[0047]   Thus, this invention provides a simple and
          efficient way to substantially remove all of N_2O prior
          to cold box in cryogenic air separation plants, thereby

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ensuring a safe operation and potentially reducing liquid oxygen drainage.

[0048]   The results of the present invention are even more surprising when evaluated in the context of the prior art selection criteria, i.e. the ratio of Henry Law constants for $N_2O/CO_2 > 0.49$ (U.S. 6,106,593). The ratio of Henry Law constants (ratio of initial isotherm slopes for N_2O/CO_2) was computed for clinoptilolite. This ratio was found to be about 0.40, well below the minimum recommended value of 6,106,593.

[0049]   The prior art solution to the problem of removing N_2O from air has focused upon finding an adsorbent with high N_2O/CO_2 selectivity; however, this is difficult DUE to the similar electrostatic properties of these two adsorbates. Further electrostatic considerations do not recognize the significant effects of the relative concentrations of the adsorbates; e.g. in ambient air, CO_2 concentrations are typically 350 ppm to 400 ppm, one thousand times that of N_2O concentrations.

[0050]   In the present invention because H_2O and CO_2 are almost completely removed prior to N_2O removal, the relevant separation is the removal of N_2O from N_2. In this case, while electrostatics favor the selectivity of N_2O, the significant concentration difference ($\sim$790,000 ppm N_2 compared to $\sim$350 ppb N_2O) favors the adsorption of N_2. Thus in accordance with the present invention the adsorbent required has high N_2O/N_2 selectivity, low N_2 working capacity and sufficient N_2O working capacity to satisfy the purification requirements.

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[0051]   In the practice of the present invention,
   adsorbent performance may be estimated by determining
   the working capacity of each of the primary adsorbates,
   i.e. N_2 and N_2O. The separation factor α, as defined
   below is utilized to evaluate the adsorbent
   effectiveness. This methodology is discussed in detail
   in US Patent 6,152,991.

$$\alpha = \frac{\Delta N_2O}{\Delta N_2} = \frac{w_{N_2O}(y,p,T)_{ads} - w_{N_2O}(y,p,T)_{des}}{w_{N_2}(y,p,T)_{ads} - w_{N_2}(y,p,T)_{des}} \qquad (1)$$

where separation factor α is defined as the ratio of
the working capacities. The numerator in this equation
is the working capacity of N_2O, which is equal to the
difference in loading w between adsorption and
desorption conditions. The adsorption and desorption
conditions are characterized by composition y, pressure
p and temperature T.

[0052]   In TSA air prepurification, maximum regeneration
   temperatures may vary from about 100°C to about 350°C.
   As a result, it is expected that the adsorbates
   (particularly atmospheric gases) will be completely
   thermally desorbed. Under such conditions, Equation (1)
   can be simplified as follows:

$$\alpha = \frac{\Delta N_2O}{\Delta N_2} = \frac{w_{N_2O}(y,p,T)_{ads}}{w_{N_2}(y,p,T)_{ads}} \qquad (2)$$

[0053]   When a contaminant is removed in a shallow
   adsorbent layer in TSA and significant resistance to

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mass transfer exists, the selectivity is redefined
according to Equation (3):

$$\frac{\Delta X_A}{\Delta X_B} = \frac{\dfrac{m_{in}}{w_s} \int_0^{t_b} (y_{in} - y_{out}) \, dt}{X_B \, (y, P, T)_{ADS}} \qquad (3)$$

The numerator in Equation (3) represents the working
capacity of the adsorbent for the contaminant. m_{in}
represents the molar feed flow into the bed, y_{in} and y_{out}
are the inlet and outlet mole fractions of the minor
component, respectively, w_s is the mass of adsorbent
and t_b is the breakthrough time corresponding to a
predetermined concentration. The denominator is the
equilibrium capacity of the major component at the
conditions at the end of the adsorption step, i.e.
assuming complete desorption of all components. This
situation may result when using small pore zeolites at
conditions where the depth of the adsorbent layer is
shorter than the mass transfer zone length.

[0054]   This method is superior to prior art methods for
evaluating the selectivity of N_2O in that the working
capacities are determined at the partial pressure of
each individual component at the relevant process
conditions. Furthermore, coadsorption effects are
incorporated in the determination of the loadings. The
analysis can be performed using either a multicomponent
isotherm model supported by pure component data (e.g.
loading ratio correlation isotherm model) or directly
from experimental data. Since the concentration of N_2
is overwhelming compared to N_2O, the coadsorption
effect of N_2O upon N_2 is negligible. Thus, the
denominator of Equation (2) or Equation (3) may be

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obtained directly from the measured pure-component N_2 isotherm.

[0055]   Conversely, the coadsorption of N_2 has a very significant effect upon the adsorption of N_2O. If accurate low concentration pure-component isotherm data for N_2O is available or attainable, then Equation (2) may be applied to assess working capacity and selectivity. Otherwise, it is preferred to determine the working capacity for N_2O directly under coadsorption conditions with N_2 using the breakthrough test method, which is well know to those skilled in the art. This allows any kinetic effects to be incorporated into the working capacity as well. The breakthrough tests allow for the determination of the equilibrium capacity of a component at saturation, and the breakthrough capacity and time at some defined breakthrough level, e.g. 50 ppb.

[0056]   In order to evaluate adsorbents for N_2O working capacity and separation factor according to Equation (3), a breakthrough test apparatus was constructed as shown in Figure 1.

[0057]   The adsorbents tested were obtained from the sources listed below. The natural adsorbents (clinoptilolite and chabazite) were obtained from Steelhead Specialty Minerals, WA. Synthetic zeolites were obtained from various manufacturers: Zeolyst (ZSM5, mordenite), Zeochem (CaX(2.5) and >85% Ca) and UOP (13X, NaX(2.3), LiX(2.3) >97% Li; LiX(2.0) >97% Li, NaY). Note that the numbers recited in the parentheses (e.g. 2.5, 2.3, and 2.0) refer to SiO_2/Al_2O_3 ratio. All of the adsorbents were thermally regenerated at 350°C, 1.0 bar pressure and under N_2 purge for approximately

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16 hours before each test. After regeneration the
adsorbents were allowed to cool to the test temperature
of 27°C.

[0058]   Breakthrough tests were conducted using the
following feed gas mixtures: 1.0 ppm N_2O in N_2 and 1.0
ppm N_2O in He. Also, N_2 isotherms were determined
gravimetrically. The results from these tests were
examined to determine N_2O separation factor and working
capacity. Tests were performed to saturation, i.e.
until the effluent N_2O concentration reached the feed
level concentration. For evaluating various
adsorbents, a N_2O concentration of 1.0 ppm was
selected. All of the breakthrough tests were performed
at 6 bar, 300 K and an inlet gas flowrate of
approximately 21.3 slpm (0.08 $kmol/m^2$ s) using an
adsorption column length of either 22.9 cm or 5.6 cm.
The feed conditions are representative of conditions at
the inlet of an air prepurifier for a typical cryogenic
air separation plant. Breakthrough curves were also
generated using 1.0 ppm N_2O in He and 1.0 ppm CO_2 in He
to determine pure-component N_2O or CO_2 loadings,
respectively. In order to determine the coadsorption
effects of N_2O and CO_2 in N_2, breakthrough tests were
also performed using 1.0 ppm N_2O + 1.0 ppm CO_2 in N_2.
Initial breakthrough was established at 50.0 ppb N_2O
and initial breakthrough loading (IBL) was determined
as the average amount of N_2O adsorbed per unit weight
of adsorbent at the 50.0 ppb breakthrough.

[0059]   Breakthrough tests are conducted in the following
manner using the apparatus shown in Figure 1. A
challenge gas from source 1 containing the
contaminant(s) of interest (e.g. 10 ppm N_2O in N_2) is

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metered through flow controller 3, and mixes in a gas mixer 5 with high purity diluent N_2 or He from source 2 and provided at a prescribed flowrate through a flow controller 4 to achieve the desired feed concentration of contaminant(s). This mixed challenge gas is then fed to the test bed 6 containing the adsorbent. The effluent is passed through a flow meter 7 to the N_2O analyzer 8 (TEI Model 46-C) where the breakthrough concentration of N_2O is monitored as a function of time. Control valve 9 is used to maintain the desired pressure in the system. The piping and adsorbent bed are maintained at the same temperature as the feed by immersing them in a thermostat bath (not shown).

The following are non-limiting examples that illustrate the methodology for selecting adsorbents and their implementation in accordance with the invention.

Example 1. N_2 Coadsorption Effects

[0060] Adsorbents were tested as described above to determine the effect of N_2 coadsorption upon the adsorption of N_2O. The results of the saturation capacity of N_2O (1.0 ppm) in N_2 and in He on various adsorbents are compared in Table 1 below. These results were determined for feed conditions of 6.0 bar, 300°K and 0.08 kmol/m^2 s molar flux using a 22.9 cm or 5.6 cm adsorbent bed length. The SiO_2/Al_2O_3 ratio is specified for some adsorbents in the table, e.g. NaX (SiO_2/Al_2O_3 =2.3). Figure 2 shows N_2O breakthrough curves for adsorbent 13X (NaX 2.5) for N_2O in N_2 and N_2O in He.

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[0061]   Table 1: Effect of N_2 Coadsorption Upon N_2O
    Loading

Material	N_2O loading (mmol/gm) 1.0 ppm N_2O/He	N_2O loading (mmol/gm) 1.0 ppm N_2O/ N_2	Preferred Adsorbents
NaY	4.06×10^{-4}	1.42×10^{-4}	
NaZSM5	1.7×10^{-3}	3.59×10^{-4}	
NaKX		4.58×10^{-4}	
13X NaX (2.5)	9.55×10^{-4}	6.09×10^{-4}	
NaX (2.3)	1.73×10^{-3}	7.03×10^{-4}	
CaX		1.98×10^{-3}	
Na-Mordenite		6.38×10^{-3}	
Clinoptilolite (CS400)	8.86×10^{-2}	3.60×10^{-3}	X
LiX (2.3)	5.5×10^{-3}	1.22×10^{-3}	X
LiX (2.0)	6.7×10^{-3}	1.74×10^{-3}	X
Chabazite	6.75×10^{-2}	3.42×10^{-3}	X
Clinoptilolite (TSM140)	6.84×10^{-2}	8.20×10^{-3}	X

[0062]   These results clearly show the substantial effect
    of N_2 coadsorption, resulting in a decrease in N_2O
    capacity from 36% to 96% compared to the single
    component saturation capacity (1.0 ppm N_2O in He). The
    fourth column of Table 1 also indicates examples of
    preferred adsorbents of the invention (i.e. adsorbents
    with high N_2O loading in the presence of N_2).

Example 2. N_2 Isotherms

[0063]   Isotherms for N_2 at 300°K were determined for
    various adsorbents over a range of pressures which
    included typical feed pressures to a prepurifier of a
    cryogenic air separation unit.   Example isotherms are
    shown in Figure 3.   The pure component N_2 loadings from

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these isotherms are compared in Table 3 for various
adsorbents at 6.0 bar.

Table 2. Equilibrium Loadings of
N$_2$ at 6.0 bar, 300°K

Material	N$_2$ loading (mmol/gm)
Silicalite	0.68
H-ZSM5	0.74
4A	1.11
NaY	0.85
NaZSM5	
NaKX	0.86
13X NaX (2.5)	1.30
NaX (2.3)	1.33
CaX	1.53
Na-Mordenite	1.40
Clinoptilolite (CS400)	0.64
LiX (2.3)	1.71
LiX (2.0)	2.29
Chabazite	1.22
Clinoptilolite (TSM140)	1.23

Example 3. Breakthrough at 50 ppb N$_2$O

[0064]   The average N$_2$O loading (IBL) of the adsorbent bed
was determined at 50.0 ppb N$_2$O from the same N$_2$O/N$_2$
tests reported in Table 1 above. Typical breakthrough
results are illustrated in Figure 4. The IBL values
(reflecting not only the 50 ppb breakthrough, but also
N$_2$ coadsorption) are compared for various adsorbents in
Table 3 and shown in Figure 5. Separation factors were
also computed using Equation 3. The N$_2$ loadings at 6
bar from Table 2 are used in Equation 3 to represent
the working capacity of N$_2$ in the process.

[0065]   N$_2$O working capacities can be computed either from
the saturation loadings of N$_2$O/N$_2$ or from the average

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loadings of N_2O at the IBL. The separation factor
computed from the average loadings at the IBL is the
preferred method since it reflects both the equilibrium
and dynamic effects of the adsorbent. Nevertheless,
the former method (which reflects equilibrium effects
only) is acceptable when only isotherms and no
breakthrough data are available. Both separation
factors are tabulated in Table 3 for various
adsorbents. Both methods identify clinoptilolite (TSM-
140) as having the highest N_2O/N_2 separation factor, as
well as establishing the same group of six adsorbents
with higher separation factors compared to the prior
art choice of CaX. The order of effectiveness amongst
the adsorbents in the preferred group is affected by
which separation factor method is used.

[0066]   Using the methodology of the invention,
clinoptilolite TSM-140 is the most preferred adsorbent
for removing N_2O from air. This adsorbent has the
highest N_2O working capacity at IBL, the highest
working N_2O/N_2 separation factor and a moderate N_2
working capacity. It is evident from Table 3 that
TSM140 has approximately 6.6 times the average N_2O
breakthrough capacity of CaX. Thus, clinoptilolite
TSM140 provides a surprisingly superior solution to the
problem.

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Table 3: IBL and α for Various Adsorbents

Material	IBL (mmol/gm)	α (Eqn 3) N$_2$O @ IBL	α (Eqn 3) N$_2$O @ 1.0ppm
Silicalite	2.20×10^{-5}	3.24×10^{-5}	1.11×10^{-4}
Activated carbon	2.60×10^{-5}		
H-ZSM5	3.60×10^{-5}	4.89×10^{-5}	1.85×10^{-4}
4A	4.30×10^{-5}	3.87×10^{-5}	
NaY	5.20×10^{-5}	6.09×10^{-5}	1.67×10^{-4}
NaZSM5	6.50×10^{-5}		
NaKX	1.32×10^{-4}	1.54×10^{-4}	5.33×10^{-4}
13X NaX (2.5)	1.87×10^{-4}	1.44×10^{-4}	4.68×10^{-4}
NaX (2.3)	2.27×10^{-4}	1.71×10^{-4}	5.29×10^{-4}
CaX	2.40×10^{-4}	1.57×10^{-4}	1.29×10^{-3}
Na-Mordenite	3.13×10^{-4}	2.24×10^{-4}	4.56×10^{-3}
Clinoptilolite (CS400)	3.56×10^{-4}	5.57×10^{-4}	5.64×10^{-3}
LiX (2.3)	3.82×10^{-4}	2.23×10^{-4}	7.10×10^{-4}
LiX (2.0)	7.68×10^{-4}	3.35×10^{-4}	7.61×10^{-4}
Chabazite	1.04×10^{-3}	8.55×10^{-4}	2.81×10^{-3}
Clinoptilolite (TSM140)	1.58×10^{-3}	1.28×10^{-3}	6.64×10^{-3}

Example 4: N$_2$O and CO$_2$ Coadsorption Effects

[0067]   In the present invention, the adsorber is preferably configured so that the water vapor and CO$_2$ contaminants in the feed air are substantially removed from the gas mixture prior to the final clean up of the stream in which N$_2$O is adsorbed. Sufficient removal of N$_2$O must be affected to prevent breakthrough beyond 50 ppb N$_2$O during the adsorption step of the prepurifier cycle. In this situation, it is estimated that low levels of CO$_2$ (less than 10.0 ppm, most likely less than 1.0 ppm) could be present with 100 ppb or more N$_2$O with the remaining bulk gas being of air composition (N$_2$/O$_2$). In order to verify the effectiveness of the adsorbent and to determine the competitive coadsorption effects of CO$_2$ upon N$_2$O, breakthrough tests were performed with clinoptilolite TSM140 using a feed

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mixture with 1.0 ppm CO_2 and 1.0 ppm N_2O in N_2. The
results are shown in Table 4 for the average IBL
loading and saturated loadings of N_2O. The loadings
are comparable within the experimental error with the
N_2O loadings from Tables 1 and 3. Thus, it is evident
that CO_2 and N_2O do not compete with each other at
these low concentrations, i.e. each competes
individually only with N_2. This can be explained by
the fact that the number of adsorbed molecules of N_2
(Table 3) is far greater than either those adsorbed
molecules of N_2O or CO_2. As N_2O or CO_2 enter the
adsorbent the adsorption sites are predominantly
occupied by N_2 molecules.

Table 4: IBL and saturation loadings(1 ppm N_2O+1 ppm

CO_2 in N_2)

IBL N_2O (mmol/gm)	N_2O saturation loading (mmol/gm)
1.6×10^{-3}	8.3×10^{-3}

[0068]   These results suggest that other low-level
contaminants present in the gas stream can also be
removed simultaneously with N_2O. In the case of
clinoptilolite, adsorbates with a kinetic diameter less
than about 4.5Å and with an interaction potential
energy greater than that of N_2 are likely to completely
or partially removed. Such adsorbates include but are
not limited to acetylene, ethylene and propane.

Example 5: Prepurifier operation
[0069]   A two-bed TSA prepurifier was designed to evaluate
the adsorbent requirement for complete N_2O removal.

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The inlet air flow was 569,000 NCFH at a pressure of 72 psig, and an ambient temperature of about 78 F. The ambient N_2O level was about 400 ppb and the CO_2 level was about 400 ppm. Average temperature of air going into the prepurifier was about 44.6 F. Each bed has an internal diameter of 8.0 ft.

[0070]   Initially the bed has two layers: First layer of Alumina (9.9 in) and the second layer of 13X APG (46.5 in). The breakthrough level of N_2O was monitored for this two-layered bed system. It was found that about 80% of the entering N_2O in each cycle is retained in the bed. About 20% of the incoming N_2O breaks through the bed. The thickness of the clinoptilolite TSM 140 layer needed to ensure complete N_2O removal if this layer is added downstream of 13 X layer was calculated to be about 9 in. Therefore, a very thin layer of clinoptilolite TSM140 added downstream of 13X layer substantially eliminates the problem of N_2O leaking into the cold box. The resulting prepurifier with the three layers could substantially eliminate all of water vapor, CO_2 and N_2O and most of the hydrocarbons entering the bed.

[0071]   The Si/Al ratio and the composition (% of exchangeable cations) of major cations in clinoptilolite TSM140 and CS400 are given in Table 5. It is evident from the working capacity in Table 1 and the selectivity in Table 3 that TSM140 has superior ability to remove N_2O in the presence of high concentrations of N_2 compared to CS400. Although both materials are of clinoptilolite structure with nearly the same Si/Al ratio, the efficiency of adsorption of N_2O is quite different. A primary difference in the

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composition of these materials is in the amount of Na
cation present. We have found that a preferred
clinptilolite would have sodium in an amount between
about 30 to about 80% of the exchangeable cations.

Table 5: Composition of natural adsorbents

	TSM140	CS400
Si/Al	4.84	4.78
% Ca	12	34
% Na	62	14
% K	19	32
% Mg	7	20

[0072]   As indicated above, clinoptilolite (most
          preferably TSM140 and CS400), chabazite and LiX (most
          preferably having a greater than 86% Li exchange and a
          SiO_2/Al_2O_3 ratio of (2.3) or (2.0)) were found to be the
          preferred adsorbents for removing N_2O from air prior to
          cryogenic air separation.

[0073]   The natural zeolites clinoptilolite and chabazite,
          having higher Si/Al ratio (3.0 to 5.0 in this
          invention) than type X zeolites, are "weaker"
          adsorbents compared to LiX, CaX and NaX. These natural
          zeolites also have a smaller micropore volume than type
          X. These factors contribute to the lower N_2 adsorption
          capacity and selectivity; however, overall capacity is
          typically not a critical issue when removing trace
          quantities of contaminants. Conversely, because of the
          higher Si/Al ratio of clinoptilolite and chabazite,
          these materials have fewer cations. This generally
          means weaker energetics in relation to polar
          adsorbates. While this favors weaker attraction for N_2
          it also means weaker attraction for N_2O as well.

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[0074]   The adsorption characteristics of zeolites are
        strongly dependent upon their cation composition. Both
        the equilibrium and kinetic adsorption properties can
        be altered by ion exchange. Cation type, location and
        number can completely alter adsorption behavior. Acid
        washing of small pore natural zeolites may remove
        impurities that block the pores, progressively
        eliminate cations and finally dealuminate the structure
        as the strength and duration of the treatment
        increases. Alkali washing has been shown to modify both
        the pore size and pore volume of clinoptilolite. The
        method and extent of dehydration is important in
        determining the adsorption properties and structural
        stability of activated zeolites. Dehydration and
        thermal treatment can result in cation migration,
        thereby influencing cation location and pore openings.
        Any of the methods may be used to further improve the
        adsorption characteristics of the preferred adsorbents
        of this invention, i.e. equilibrium and/or kinetic
        adsorption properties may be effected.

[0075]   As indicated previously, the invention relates to
        the removal of N_2O from air in which the H_2O and CO_2
        have already been substantially removed. By
        "substantially removed" we mean removed to levels of
        less than 10ppm, preferably less than 1.0 ppm.
        However, the invention may be applied in removing N_2O
        in the presence of higher concentrations of CO_2 and/or
        H_2O. In the most direct application of the invention,
        a layer of the N_2O-selective adsorbent is located
        downstream (as determined by the direction of feed flow
        during adsorption) of those adsorbents that are used to
        remove H_2O and CO_2. Typical TSA prepurifiers have

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either a single layer of zeolite to remove both H_2O and CO_2 or a layer of activated alumina (for H_2O removal) followed by a layer of zeolite for CO_2 adsorption. In general, adsorbents useful for the water and CO_2 adsorption are known to those skilled in the art and include cation containing zeolites (synthetic or natural), activated alumina, silica gel and activated carbon.

[0076]   In such configurations, the N_2O-selective layer would represent either a second or third layer of adsorbent, respectively, in the prepurifier adsorber. Other alternative configurations contemplated by this invention are described below. According to the invention N_2O is adsorbed onto at least one adsorbent selected from natural clinoptilolite, natural chabazite and Li exchanged X zeolite. The removal of N_2O from the gas stream is achieved by passing the gas stream through a bed of clinoptilolite, chabazite or LiX or a mixture of these in the temperature range of about - 70°C to 80°C, preferably 0°C to 40°C. While the invention is directed at the removal of low concentrations of N_2O from air, it may also be used to remove higher concentrations of N_2O from air or other gas mixtures. Typical gases that can be purified by this process include air, nitrogen, oxygen, argon, methane etc.

[0077]   The process of N_2O removal is carried out preferably in a cyclic process such as pressure swing adsorption (PSA), temperature swing adsorption (TSA), vacuum swing adsorption (VSA) or a combination of these. Such processes can be used for removing ppm or ppb levels of N_2O present in air prior to cryogenic

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separation.   The process of the invention may be
carried out in single or multiple adsorption vessels
operating in a cyclic process that includes at least
the steps of adsorption and regeneration. The
adsorption step is carried out at pressure range of 1.0
to 25 bar and preferentially from about 3 to 15 bar.
The temperature range during the adsorption step is -
70°C to 80°C. When a PSA process is used, the pressure
during the regeneration step is lower than the
adsorption pressure, preferably in the range of about
0.20 to 10.0 bar, and preferably 1.0 to 2.0 bar. For a
TSA process, regeneration is carried out at a
temperature greater than the adsorption temperature;
preferably in the range of about 50°C to 400°C, more
preferably between 100°C to 300°C. In cryogenic air
separation processes, the regeneration gas is typically
taken from the product or waste N_2 or O_2 streams.

[0078]   In the cyclic process, the gas containing N_2O is
            introduced at one end of an adsorption vessel that
            contains at least a layer of N_2O-selective adsorbent.
            As the gas passes through the bed, N_2O is adsorbed and
            an essentially N_2O-free gas is obtained at the other
            end of the bed. As the adsorption step proceeds, a N_2O
            front develops in the bed and moves forward through the
            bed during the adsorption step. When the front reaches
            the end of the bed, which is determined by the
            concentration of N_2O acceptable in the outlet gas, the
            adsorption step is terminated and the vessel enters the
            regeneration mode. The method of regeneration depends
            upon the type of cyclic process. For a PSA process,
            generally the vessel is countercurrently depressurized.
            Subatmospheric pressure levels can be additionally

employed during the regeneration steps using a vacuum
pump. For a TSA process, regeneration of the adsorbent
bed is achieved by passing heated gas countercurrently
through the bed. Using the thermal pulse method, a
cooling purge step follows the hot purge step. The
heated regeneration gas may also be provided at a
reduced pressure (relative to the feed) so that a
combined TSA/PSA process is affected. For removal of
N_2O from air, the TSA/PSA method is preferred.

[0079]   In some cases, passing an inert or weakly adsorbed
purge gas countercurrently through the bed can further
clean the adsorbent bed. In a PSA process, the purge
step usually follows the countercurrent
depressurization step. In a TSA process, the heated
purge gas can be used for regeneration of adsorbent. In
case of a single vessel system, the purge gas can be
introduced from a storage vessel, while for multiple
bed system, purge gas can be obtained from another
adsorber that is in the adsorption phase.

[0080]   The adsorption system can have more steps than the
two basic fundamental steps of adsorption and
desorption. For example, top to top equalization or
bottom to bottom equalization can be used to conserve
energy and increase recovery.

[0081]   In a specific embodiment, the prepurification
process operates as follows with reference to Fig. 6.
Referring to Figure 6, feed air fed to the system via
conduit 23 is compressed in compressor 10 and cooled by
chilling means 11 prior to entering one of two
adsorbers (16 and 17) where at least the contaminants
H_2O, CO_2 and N_2O are removed from the air. The purified
air exits the adsorber via conduit 24 and then enters

the air separation unit (ASU) (not shown) where it is
then cryogenically separated into its major components
N_2 and O_2. In special designs of the ASU, Ar, Kr and
Xe may also be separated and recovered from the air.
While one of the beds is adsorbing the contaminants
from air, the other is being regenerated using purge
gas provided via conduit 25. A dry, contaminant-free
purge gas may be supplied from the product or waste
stream from the ASU or from an independent source to
desorb the adsorbed contaminants and thereby regenerate
the adsorber and prepare it for the next adsorption
step in the cycle. The purge gas may be N_2, O_2, a
mixture of N_2 and O_2, air or any dry inert gas. In the
case of thermal swing adsorption (TSA), the purge gas
is first heated in heater 22 prior to being passed
through the adsorber in a direction countercurrent to
that of the feed flow in the adsorption step. TSA
cycles may also include a pressure swing. When only
pressure swing adsorption (PSA) is utilized, there is
no heater.

[0082]   The operation of a typical PSA cycle is now
described in reference to Figure 6 for one adsorber.
One skilled in the art will appreciate that the other
adsorber vessel will operate with the same cycle, only
out of phase with the first adsorber in such a manner
that purified air is continuously available to the ASU.
Feed air is introduced via conduit 23 to compressor 10
where it is pressurized. The heat of compression is
removed in chilling means 11, e.g. a mechanical chiller
or a combination of direct contact after-cooler and
evaporative cooler. The pressurized, cool and H_2O-
saturated feed stream then enters adsorber 16. Valve

12 is open and valves 14, 18 and 20 are closed as the
adsorber vessel 16 is pressurized. Once the adsorption
pressure is reached, valve 18 opens and purified
product is directed to the ASU with conduit 25for
cyrogenic air separation. When the adsorber 16 has
completed the adsorption step, valves 18 and 12 are
closed and valve 14 is opened to blow down the adsorber
16 to a lower pressure, typically near ambient
pressure. Once depressurized, valve 20 is opened and
heated purge gas is introduced into the product end of
the adsorber 16. At some time during the purge cycle,
the heater is turned off so that the purge gas cools
the adsorber to near the feed temperature.

[0083]   One of ordinary skill in the art will further
appreciate that the above description represents only
an example of a typical prepurifier cycle, and there
are many variations of such a typical cycle that may be
used with the present invention. For example, PSA may
be used alone wherein both the heater 22 and the
chilling means 11 may be removed. Pressurization may
be accomplished with product gas, feed gas or a
combination of the two. As indicated above, bed-to-bed
equalization may also be used and a blend step may be
incorporated where a freshly regenerated bed is brought
on line in the adsorption step with another adsorber
nearing completion of its adsorption step. Such a
blend step serves to smooth out pressure disturbances
due to bed switching and also to minimize any thermal
disturbances caused when the regenerated bed is not
completely cooled to the feed temperature.
Furthermore, the invention may be practiced with a
prepurifier cycle not limited to two adsorber beds.

[0084]   As indicated above, the most preferred embodiment
of the present invention is the removal of trace
amounts of N_2O from gaseous streams, particularly from
air prior to cryogenic separation. The method of the
invention is particularly applicable to the removal of
low to intermediate (e.g. ppb to ppm) concentrations of
N_2O from a feed stream. For example, the methodology is
particularly useful in air prepurification (prior to
cryogenic distallation) where the N_2O concentration is
on the order of 350ppb. The adsorbents are also
especially effective for the removal of N_2O from gas
streams containing 100ppm or less N_2O. If the gas
contains water vapor, this should most preferably be
removed to a level of less than 100 ppb prior to
passing it through the N_2O adsorbent. If the gas
contains CO_2, CO_2 should be removed to levels less than
10 ppm, preferably less than 1ppm, however, removal of
CO_2 is not as essential as removal of water vapor. The
relative thickness of the N_2O layer depends upon the
pressure, temperature, composition and flow of the feed
gas and the desired purity of the purified gas, but
could be determined by one of ordinary skill in the
art.

[0085]   As indicated above, in a preferred air
prepurification embodiment of the invention, water
vapor and CO_2 are substantially removed from air on at
least one layer of activated alumina or zeolite, or by
multiple layers of activated alumina and zeolite prior
to passing the air stream through the N_2O adsorbent
layer. Optionally, the N_2O-selective adsorbent layer
may be extended and used to remove part or all of the
CO_2 from air. Alternately, in an adsorption vessel, a

first layer of alumina can be used to remove water vapor and a next layer comprised of a mixture of the N_2O-selective adsorbent and 13X (or other zeolite) can be used to remove both CO_2 and N_2O from the air. Such an adsorbent mixture may be composed of physically separate adsorbents or of different adsorbents bound together in the form of a composite. Additionally, the N_2O slective adsorbent may be deposited in the form of fine particles on a substrate such as a monolith.

[0086]   In the existing prepurifier beds with water adsorbent layer and CO_2 adsorbent layer, the method of the invention allows for replacing 10-100% of CO_2 adsorbent layer with the N_2O adsorbent at the most downstream end.

[0087]   As illustrated in Figs. 7a and 7b various layered arrangements of a bed 30 are possible. Figure 7a shows for example a bed 30 arrangement comprising a layer of a first adsorbent for water removal 31; a layer 32 of a second adsorbent for CO_2 removal; and a third layer 33 that is the N_2O adsorbent.

[0088]   In Figure 7b, a bed 30 arrangement having a first layer of water adsorbent 31', and a second layer 34 that is a mixture or composite of a CO2 adsorbent and the N_2O adsorbent

[0089]   Some chemically modified forms of the adsorbents used in the process of this invention would also be appropriate for N_2O removal purposes. Thus, the method of the invention can be carried out wherein said clinoptilolite and chabazite are natural or synthetic, and have exchangeable cations from ions of Group 1A, Group 2A, Group 3A, Group 3B, the lanthanide series of the Periodic Table, as well as mixtures of these.

According to the invention, at least nitrous oxide gas
contained in a gas stream is separated, whereby N_2O is
adsorbed on at least one adsorbent or a mixture of
these selected from the following: natural
clinoptilolite, natural chabazite and Li exchanged X
zeolite. The mixture can be made with any ratio of
these adsorbents namely 0-100% clinoptilolite, 0-100%
chabazite and 0-100% LiX, wherein the total of these is
100%.

[0090]   The adsorbent beds used in the method of the
invention can have variety of configurations such as
vertical beds, horizontal beds or radial beds and can
be operated in a pressure swing adsorption mode,
temperature swing adsorption mode, vacuum swing
adsorption mode or a combination of these.

[0091]   Clinoptilolite has excellent thermal stability at
very high temperatures up to 700°C. Thus, it can be
regenerated at very high temperatures if needed.

[0092]   Since clinoptilolite and chabazite are natural
zeolites mined from the earth, they should be thermally
treated before being used in the method of the
invention. These natural zeolites should also be ground
to a suitable average grain size, for example, 4 to 50
mesh, preferably 8 to 12 mesh (US Sieve Series),
although smaller or larger average sizes may be
employed depending upon the requirements of the
application.

[0093]   In the method of the invention, the ground
natural mineral with predetermined grain size
distribution is thermally treated at a temperature of
250°C to 700°C. It is important to dehydrate the
zeolites to less than 1.0 % (wt) H_2O. Those skilled in

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the art are familiar with such sizing and calcination procedures.

[0094]   The adsorbents in this method may be shaped by a series of methods into various geometrical forms such as beads and extrudates. This might involve addition of a binder to zeolite powder in ways very well known to prior art. These binders might also be necessary for tailoring the strength of the adsorbents. Binder types and shaping procedures are well known to prior art and the current invention does not put any constraints on the type and percentage amount of binders in the adsorbents.

[0095]   The N_2O adsorbent could also potentially adsorb some hydrocarbons from air. To ensure complete removal of hydrocarbons, the N_2O adsorbent can be physically mixed in a layer 35 with a hydrocarbon selective adsorbent such as 5A (Bed 30 in Figure 7c). Alternately, an additional layer of hydrocarbon selective adsorbent can be placed upstream (layer 36) or downstream (not shown) of the N_2O adsorbent layer 33'' (Bed 30 in Figure 7d). Note that 31'' and 31''' refer to a layer of water adsorbent and 32' and 32'' refer to a layer of CO_2 adsorbent in Figures 7c and 7d respectively.

[0096]   The term "comprising" is used herein as meaning "including but not limited to", that is, as specifying the presence of stated features, integers, steps or components as referred to in the claims, but not precluding the presence or addition of one or more other features, integers, steps, components, or groups thereof.

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[0097]   Specific features of the invention are shown in
       one or more of the drawings for convenience only, as
       each feature may be combined with other features in
       accordance with the invention. Alternative embodiments
       will be recognized by those skilled in the art and are
       intended to be included within the scope of the claims.

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What is claimed is:

[0001]   1.   An adsorption process for the removal of N$_2$O
          from a gas containing N$_2$O, nitrogen and other
          components, said process comprising passing said gas
          over a bed of one or more adsorbents and producing a
          purified gas, wherein said one or more adsorbents is
          selected from the group consisting of clinoptilolite,
          chabazite and Li-exchanged zeolite.

[0002]   2.   The process of claim 1, wherein said gas is
          air.

[0003]   3.   The process of claim 1, wherein said other
          components include water and CO$_2$.

[0004]   4.   The process of claim 1, wherein said N$_2$O is
          in said gas in an amount of less than 100ppm.

[0005]   5.   The process of claim 3, wherein said water
          and said CO$_2$ are adsorbed on an additional adsorbent
          prior to said gas passing over said clinoptilolite,
          chabazite or said Li-exchanged zeolite.

[0006]   6.   The process of claim 1, wherein said gas is
          air.

[0007]   7.   The process of claim 1, wherein said process
          is either pressure swing adsorption or temperature
          swing adsorption.

[0008]   8.   The process of claim 1, wherein said process
          is a combination of temperature swing adsorption and
          pressure swing adsorption.

[0009]   9.   The process of claim 5, wherein at least 90%
          of the N_2O in said gas is adsorbed.

[0010]   10. The process of claim 1, wherein said
          adsorbent is clinoptilolite, and wherein between 30%
          and 80% of its exchangeable cations are sodium cations.

[0011]   11. The process of claim 1, wherein said
          adsorbent has been washed with an acid or alkali
          solution prior to being placed in said bed.

[0012]   12. The process of claim 1, wherein said Li-
          exchanged zeolite is LiX.

[0013]   13. The process of claim 1, wherein said product
          gas contains less than 100ppb of N_2O.

[0014]   14. The process of claim 1, wherein said product
          gas contains less than 50ppb of N_2O.

[0015]   15. The process of claim 1, wherein said product
          gas contains less than 10ppm of N_2O.

[0016]   16. The process of claim 8, wherein in said
          pressure swing adsorption process, adsorption takes
          place at a pressure between 1.0 to 25 bar, and
          desorption takes place at a pressure between 0.2 to
          10.0 bar.

[0017]   17.   The process of claim 8, wherein in said
         temperature swing adsorption process, adsorption takes
         place at a temperature between -70 degrees Celsius and
         80 degrees Celsius, and desorption takes place at a
         greater temperature than said adsorption.

[0018]   18.   A process for the separation of N2O from a
         gas stream containing at least N_2O and nitrogen, said
         process comprising passing said gas stream over a bed
         of adsorbent having a ΔN_2O working capacity of greater
         than or equal to 3.56 x 10^{-4} at IBL.

[0019]   19.   The process of claim 18, wherein said gas
         stream is air.

[0020]   20.   The process of claim 18, wherein said
         adsorbent is selected from the group consisting of
         clinoptilolite, chabazite and Li-exchanged zeoliteor
         combinations thereof.

[0021]   21.   The process of claim 18, wherein said gas
         stream contains less than 100ppm N_2O.

[0022]   22.   The process of claim 18, wherein the $\Delta N_2O/\Delta N_2$
         selectivity is greater than or equal to 2.23 x 10^{-4} at
         IBL.

[0023]   23.   An adsorption apparatus for the removal of
         N_2O from a gas containing N_2O, nitrogen and other
         components, said apparatus comprising one (30) or more

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beds of at least a first adsorbent, wherein said first
adsorbent is an N_2O selective adsorbent selected from
the group consisting of clinoptilolite, chabazite and
Li-exchanged zeolite or combinations thereof.

[0024]   24.   The apparatus of claim 23, wherein said other
components include H_2O and CO_2, and said apparatus
further contains one or more additional adsorbents for
the adsorption of H_2O and CO_2, and wherein said
additional adsorbents are upstream of said first
adsorbent.

[0025]   25.   The apparatus of claim 24, wherein said
additional adsorbents are one or more of cation
exchanged natural zeolites, cation exchanged synthetic
zeolites, alumina, silica gel and activated carbon.

[0026]   26.   The apparatus of claim 24, wherein said N_2O
selective adsorbent is in a separate layer from said
additional adsorbents.

[0027]   27.   The apparatus of claim 23, wherein said
apparatus comprises a layer of alumina and a mixed
layer of said N_2O selective adsorbent and an adsorbent
selective for CO_2 downstream of said layer of alumina.

[0028]   28.   The apparatus of claim 23, wherein said
apparatus comprises a layer of alumina and, downstream
therefrom, a layer of a composite material comprising
said N_2O selective adsorbent and an adsorbent selective
for CO_2 bound into a single particulate material.

[0029]   29.   The apparatus of claim 23, wherein said additional adsorbents are in separate layers.

[0030]   30.   The apparatus of claim 23, wherein said adsorbent is in the form of particles having an average size that is selected between 4-50 mesh.

[0031]   31.   The apparatus of claim 23, wherein said apparatus contains two beds (16, 17).

[0032]   32.   The apparatus of claim 1, wherein said one or more beds contain a second additional adsorbent for the removal of hydrocarbons.

[0033]   33.   The apparatus of claim 32, wherein said second additional adsorbent is either in its own layer, or is mixed with said first adsorbent(s).

[0034]   34.   The apparatus of claim 23, wherein the combination of said first adsorbents is either in the form of a mixture of adsorbents or a composite adsorbent.

[0035]   35.   The apparatus of claim 23, wherein said first adsorbents are clinoptilolite and chabazite, and wherein said clinoptilolite and chabazite are either hatural or synthetic and have exchangeable cations selected from the group consisting of cations of Group 1A, Group 2A, Group 3A, Group 3B, the lanthanide series and combinations thereof.

[0036]   36.   The apparatus of claim 23, wherein said
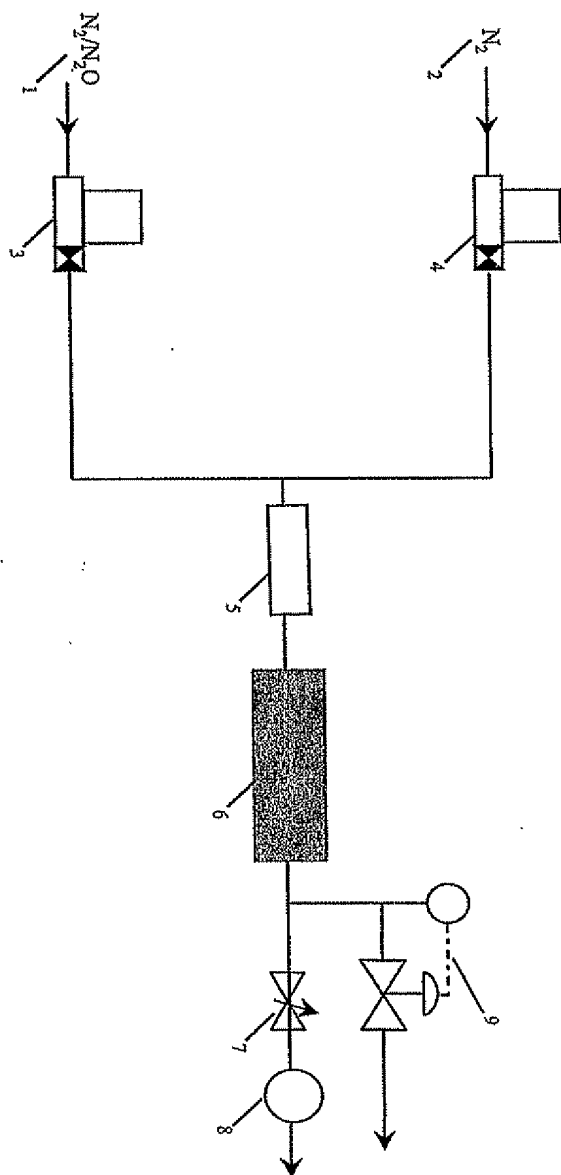   apparatus is an air prepurifier.

Figure 1
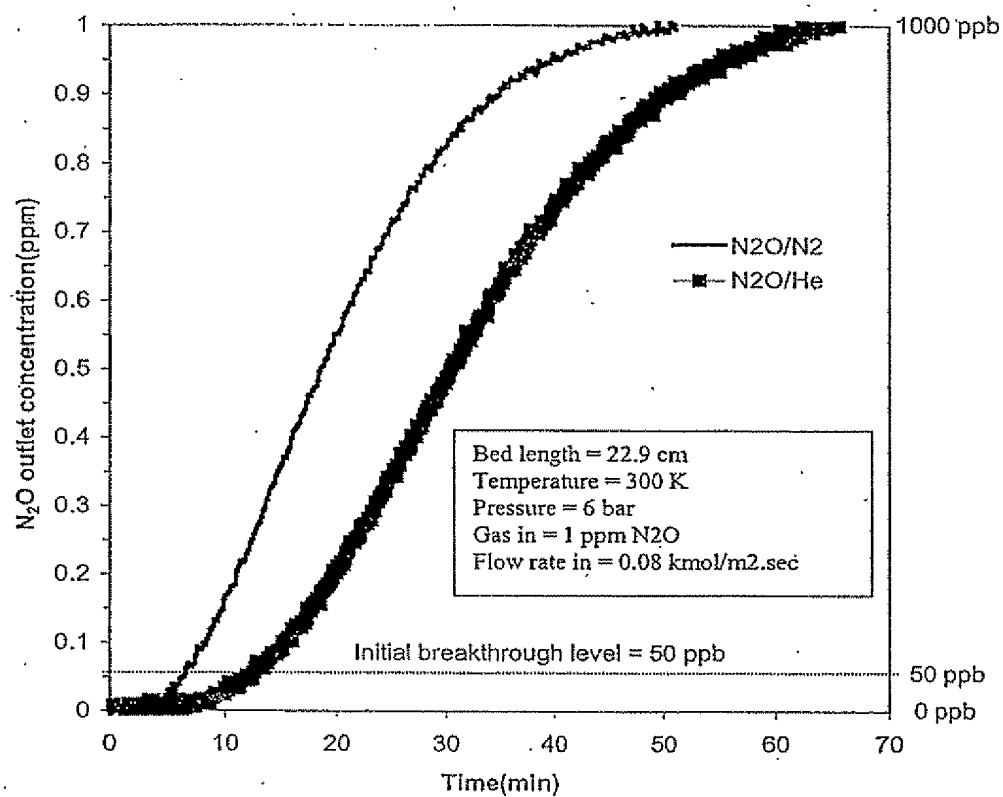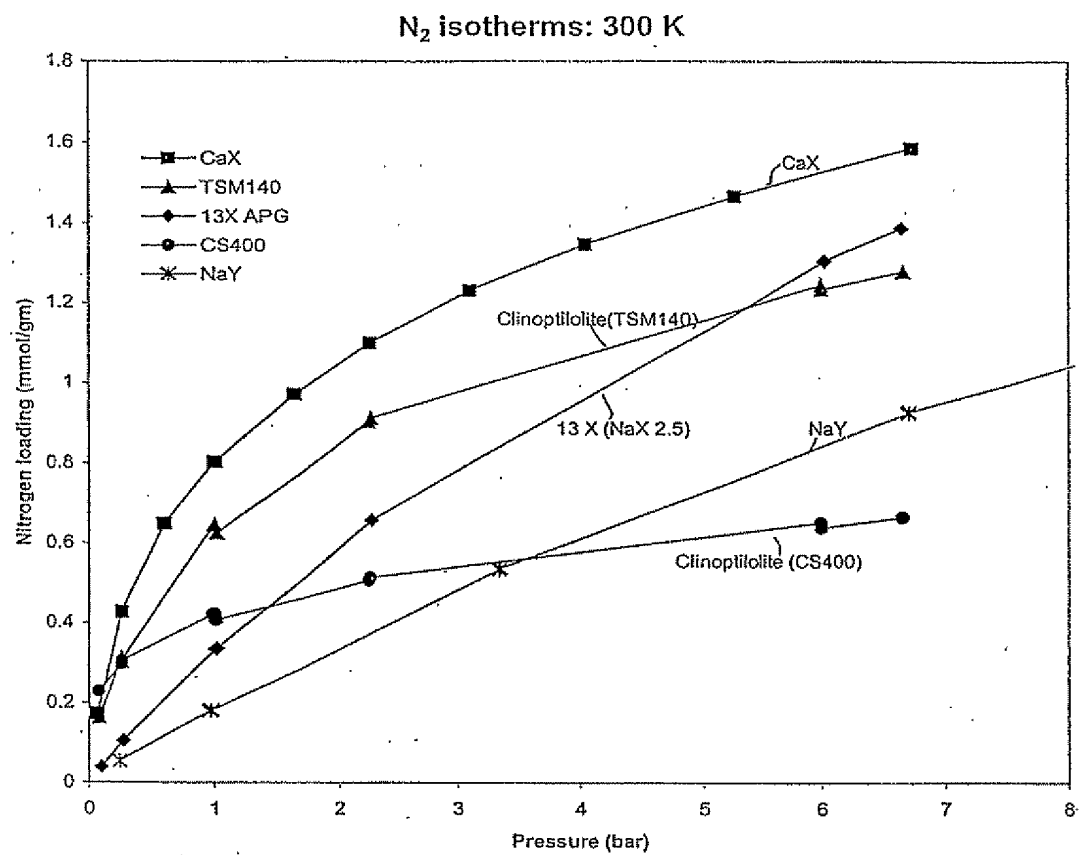
Figure 2

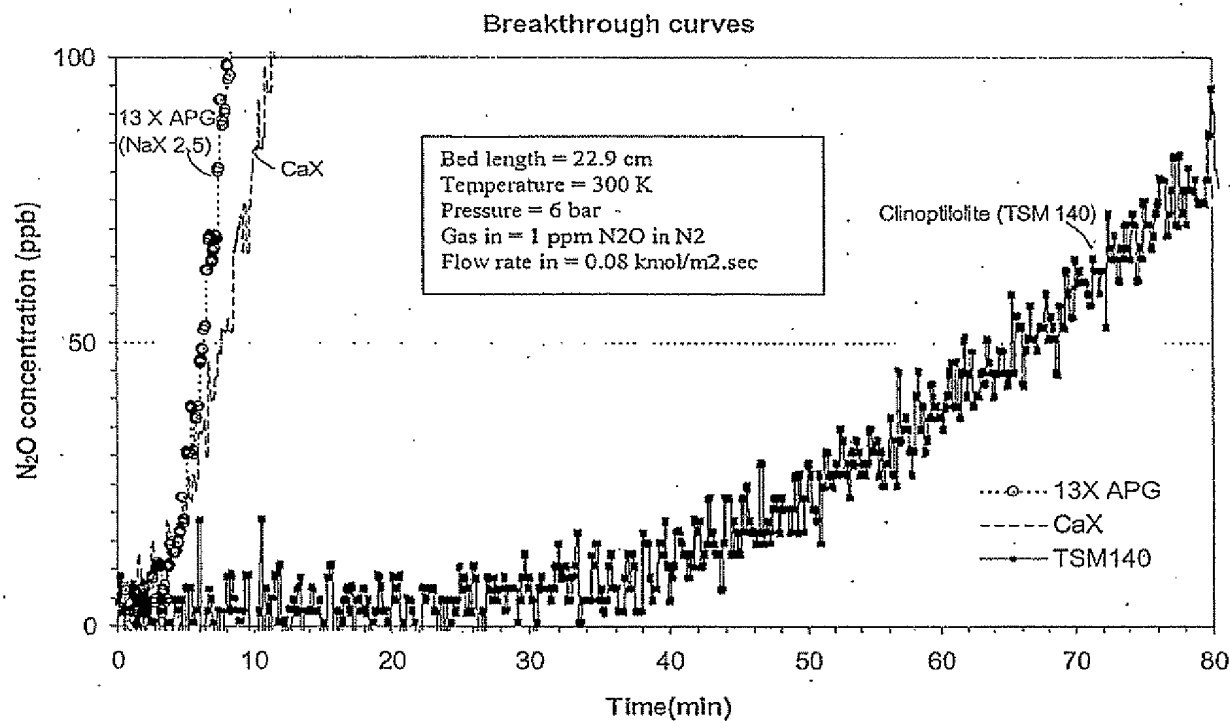## N$_2$ isotherms: 300 K

Figure 3.

Breakthrough curves
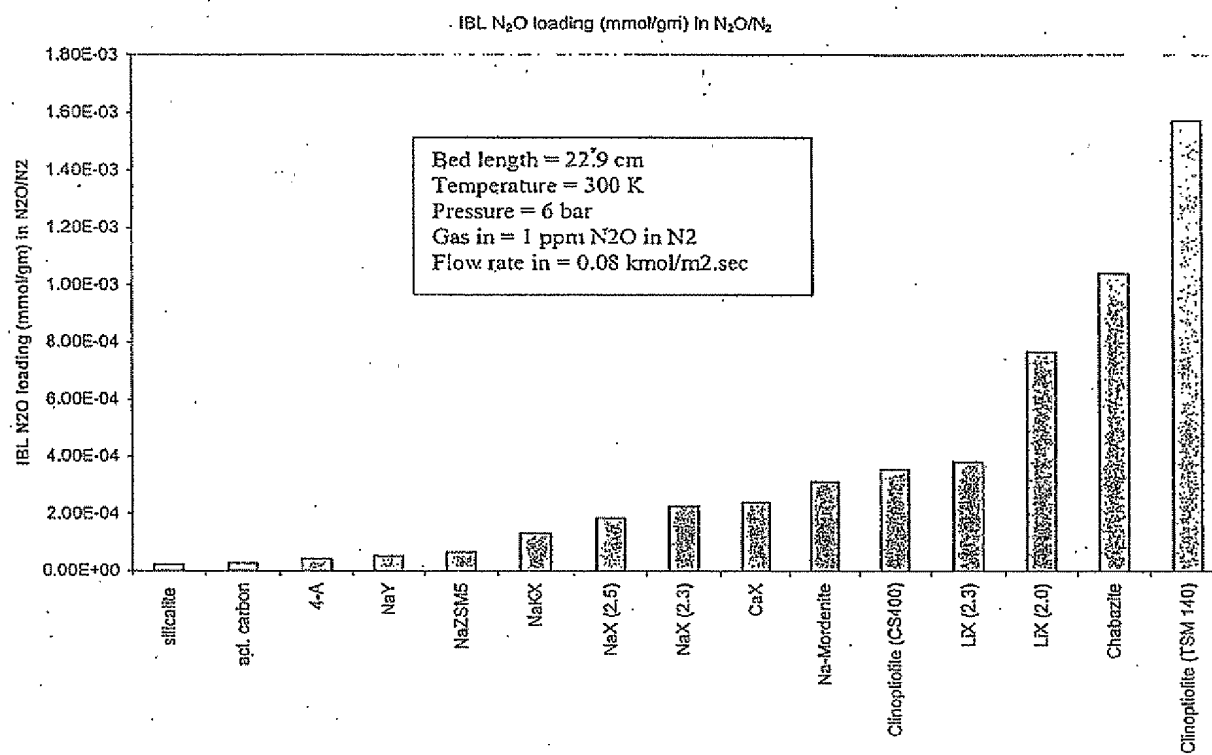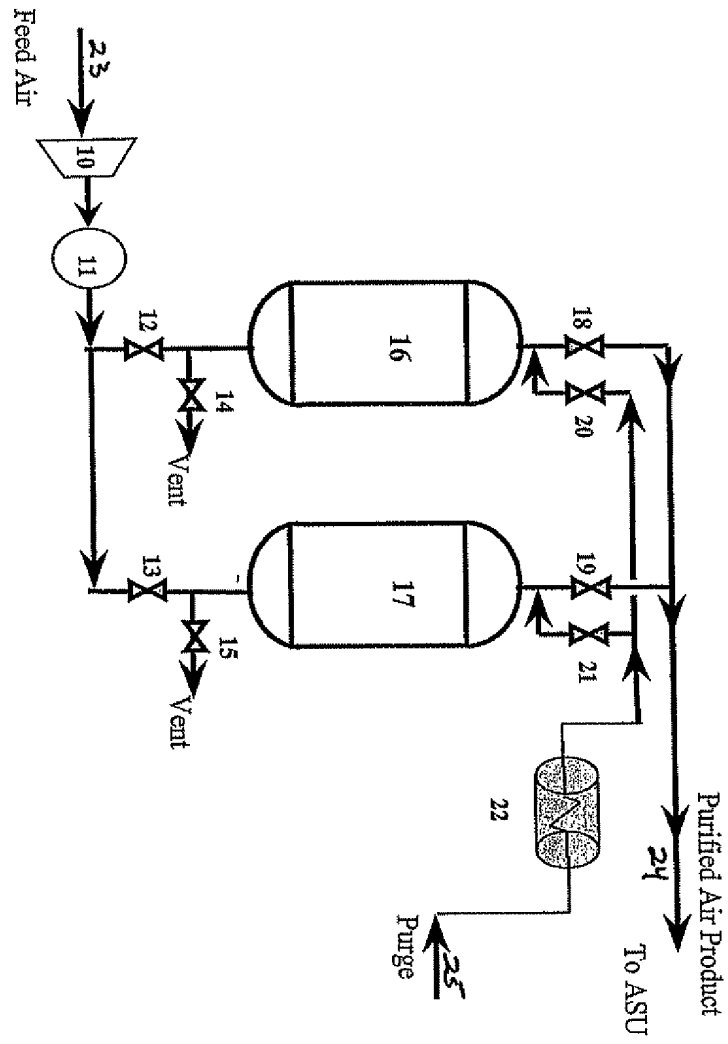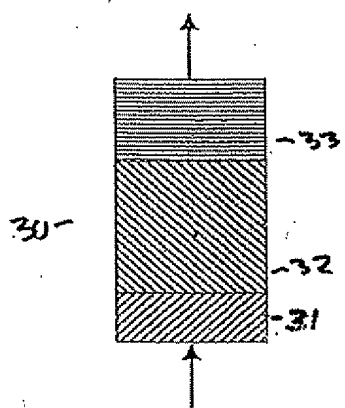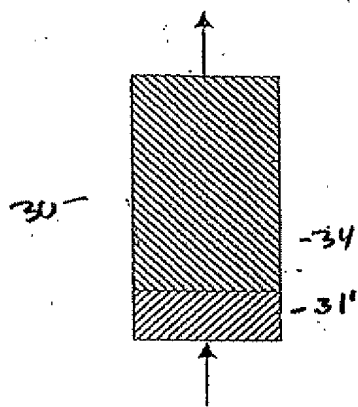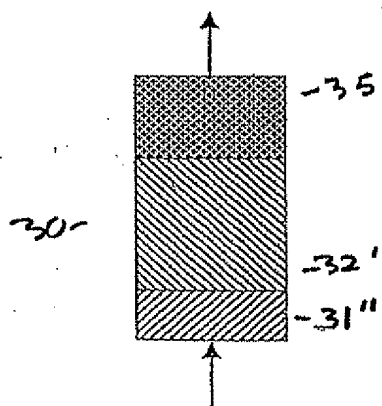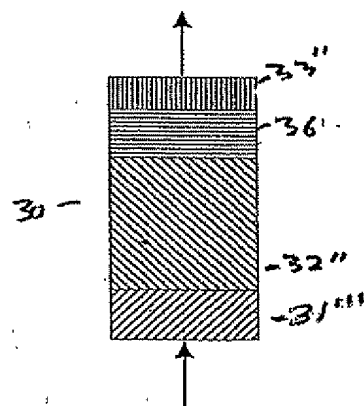
Figure 4

Figure 5.

Figure 6.

Figure 7

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B01D 53/047

US CL : 95/96,106,119,123,129,139,902; 96/130,132

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
    U.S. : 95/96-106,117-120,123,129,139,902; 96/130-133,143,144

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,507,271 A (VAN DEYCK et al.) 26 March 1985 (26.03.85).	1-36
A	US 4,933,158 A (ARITSUKA et al.) 12 June 1990 (12.06.90).	1-36
A	US 4,935,580 A (CHAO et al.) 19 June 1990 (19.06.90).	1-36
A	US 4,964,889 A (CHAO) 23 October 1990 (23.10.90).	1-36
A	US 5,587,003 A (BULOW et al.) 24 December 1996 (24.12.96).	1-36
A	US 5,919,286 A (GOLDEN et al.) 06 July 1999 (06.07.99).	1-36
A	US 5,938,819 A (SEERY) 17 August 1999 (17.08.99).	1-36
A	US 6,106,593 A (GOLDEN et al.) 22 August 2000 (22.08.00).	1-36
A,P	US 6,358,302 B1 (DENG et al.) 19 March 2002 (19.03.02).	1-36

☒ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"E"	earlier application or patent published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
01 April 2003 (01.04.2003)	01 MAY 2003
Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703)305-3230	Authorized officer
Robert H. Spitzer
Telephone No. 703-308-3794

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INTERNATIONAL SEARCH REPORT

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	US 6,391,092 B1 (SHEN et al.) 21 May 2002 (21.05.02).	1-36